

METHANOL: CLATHRATE HYDRATE FORMER OR INHIBITOR ?*

Hirokazu Nakayama^{aa}, Darren H. Brouwer^a, Y. Paul Handa^b, Dennis D. Klug^a, John S. Tse^a, Christopher I. Ratcliffe^a, Xu Zhu^a and John A. Ripmeester^{a†}

^aSteele Institute for Molecular Sciences, ^bInstitute for Chemical Processing and Environmental Technology, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Keywords: methanol, hydrate, methanol monohydrate, hydrate inhibitor, clathrate hydrate

INTRODUCTION

Methanol has long been in use as an inhibitor of hydrate formation¹. It acts as a classical antifreeze, that is by lowering the activity of the water, and generally shifts the equilibrium lines for hydrate formation in the phase diagram to lower temperatures. It has been shown that in water - hydrate former - methanol systems the methanol is excluded from the clathrate hydrate when the material is frozen². From a molecular point of view, one may argue that methanol interacts strongly with water by hydrogen bonding, thus interfering with the structure formation required for the formation of solid ice and ice-like lattices. Thus, methanol is one of few small molecules that do not form clathrate hydrates at ordinary temperatures (~ 0°C). The propensity for small water-soluble molecules to form hydrates depends on a balance between hydrophobic and hydrophilic interactions, as many of the water soluble ethers readily form clathrate hydrates³. Ethanol is known to form two different hydrates⁴ at low temperatures which are probably semi-clathrates structurally related to Str.I and Str.II hydrates (Pm3m, a=11.88 Å, F4₃₂, a=17.25 Å respectively). Isopropanol, t-butanol and iso-amyl alcohol all are known to form double hydrates with small help-gas molecules⁵.

In 1991, a report appeared⁶ which suggested that methanol, when co-deposited with water in a vacuum at low temperatures, forms a clathrate hydrate of structure II with a lattice constant of 16.3 Å. This observation poses a number of questions regarding the ability of methanol to both inhibit and promote hydrate formation. If one is a high temperature property, and the other a low temperature property, at which temperature do they cross over and what are the responsible interactions ? On the other hand, there are some general questions regarding the interpretation of the results. For instance, the usual structure II lattice parameter is 17.1 ± 0.1 Å⁷, so it isn't easy to see how the structure II lattice can adapt to a ~ 12% volume reduction.

Also, size considerations alone would suggest that methanol (an ethane-sized molecule) should form a structure I rather than a structure II hydrate. As noted above, the larger (propane-sized) ethanol molecule apparently forms semi-clathrates similar to both str. I and str II. In this sense it is pertinent to note that calculations have been performed on a str. I hydrate lattice containing methanol guests⁸. A third point is that the report does not acknowledge the possible presence of methanol monohydrate, which was reported in a study of the methanol -water phase diagram in 1961⁹. These questions led us to have a close look at the low temperature behaviour of the methanol - water system.

EXPERIMENTAL

Methanol and water were co-deposited from metered amounts of the vapours on the cold plate (~ 20K) of a Displex closed cycle refrigerator. Sample stoichiometry was varied from 20:1 to 1:1. Pure amorphous ice and methanol phases were prepared as well. Samples were handled and stored under liquid nitrogen. Some samples of a 1:1 stoichiometry were prepared by direct mixing of the liquids followed by quenching to 77K and annealing above the eutectic temperature at ~ 150K.

Sample characterization was carried out by differential scanning calorimetry (DSC), powder X-ray diffraction (XRD) and NMR spectroscopy. Samples for NMR were isotopically enriched in ²H for either the water or methanol phases.

Thermal events were recorded by means of a Tian Calvet heat-flow calorimeter (Setaram, Model BT2.15). The details of the calorimeter and the operating procedure have been described previously¹⁰. A sample size of about 2 g was used, the sample temperature always remaining below 80K during loading. Samples were scanned from 78K to room temperature at 10 K°/h with nitrogen at 200 mbar as heat exchange gas. XRD measurements were performed on a Rigaku Θ - Θ powder diffractometer equipped with a Paar temperature controller. Samples were loaded cold, and XRD

patterns were taken at 80K. Samples were annealed for 10 min. at the appropriate temperatures then cooled for the recording of the XRD pattern. The various phases which appear on crystallization of the amorphous deposits and mixtures were identified by comparison with data obtained for the pure crystalline materials or from literature data.

^2H NMR powder patterns were recorded at a frequency of 30 MHz on a Bruker MSL 200 NMR spectrometer equipped with a 5mm solenoid probe. Quadrupole echo sequences were used with a 90° pulse length of $\sim 2.5 \mu\text{sec}$ and an echo delay time of $30 \mu\text{sec}$. Samples of 1:1 stoichiometry were quenched and conditioned in the probe at temperatures somewhat above 150K. Quadrupole coupling parameters were determined by a fitting procedure using the Bruker Winfit package.

RESULTS AND DISCUSSION

Table 1 offers a summary of the calorimetric data which was obtained for a range of samples which reasonably well cover the methanol-water phase diagram. The column on the left is in good agreement with previously reported work on vapour-deposited ice. We note that all starting materials are amorphous, and that the first event to take place on warming is crystallization, or crystallization preceded by a glass transition. This is in agreement with the reported phase diagram, where devitrification is reported to take place between 110 and 120K. We note that it doesn't seem to matter much whether samples are produced by quenching the liquid mixture, or by vapour deposition.

A critically important component of the work is to identify the phases present in the low temperature region, that is after the glass transition/crystallization events. The XRD patterns of Ice Ih, Ice Ic and the clathrate hydrates are well documented. XRD patterns for the α and β phases of methanol were recorded in order to be able to recognize the presence of these phases.

In all of the experiments carried out, it was found that a number of reflections appeared which could not be assigned to one of the aforementioned crystal phases. These reflections appeared to be strongest for samples approaching a composition of 1:1 methanol/ water. Another experiment showed that these reflections disappeared when the sample was warmed to 175K, leaving only the Ice Ih pattern, but reappeared on cooling. We can conclude that these reflections should be assigned to the methanol monohydrate which is known to melt incongruently at $\sim 171\text{K}$. Although methanol monohydrate has been known to exist for many years, so far no information is available on its structure. In order to facilitate further study, a good sample of methanol monohydrate was prepared by quenching a 1:1 mixture of methanol and water and annealing at 150K for 10 hrs. The sample still contained a significant quantity of hexagonal ice as impurity, however, the remaining 19 reflections could be indexed in terms of tetragonal Laue symmetry and a fit of the d spacings was obtained with unit cell dimensions of $a = 4.660(1)$, $c = 13.813(5) \text{ \AA}$.

With the identification of the methanol monohydrate phase, all of the reflections can be accounted for for all of the samples considered in this study. The crystallization processes which transform the lowest temperature amorphous phases are outlined below for a range of sample compositions.

Ice \Rightarrow Ice Ic

methanol/water (1:20, 1:10) \Rightarrow methanol monohydrate + Ice Ih + Ice Ic (trace)

methanol/water (1:2) \Rightarrow methanol monohydrate + Ice Ih + methanol

methanol \Rightarrow α - methanol

Perhaps the most unusual observation is the near disappearance of cubic ice as a distinct phase in the presence of methanol. Figure 1 shows a typical XRD run on a codeposit (1:2 methanol- water) initially annealed at 120K. The ice Ih reflections clearly are present for all temperatures. The calorimetric data is in agreement with this, as the only evidence for the crystallization of cubic ice is from a very weak exotherm near 148K in the 10:1 deposit (see table 1), and the subsequent transformation of ice Ic to ice Ih occurs near 179K; these events occur near 142K and 195K for pure ice. Methanol seems to act as a catalyst in the direct conversion of amorphous ice to ice Ih.

How do our results relate to those reported for the " methanol clathrate " 6 ? The material prepared was thought to be a clathrate mixed with some cubic ice based on the assignment of 10 reflections to a 16.3 \AA clathrate lattice plus 1 reflection due to cubic ice. By comparing the diffraction data for the two studies it becomes apparent that all of the observed reflections in both studies can be accounted for in terms of ice

1h and methanol monohydrate. It should be noted that the small angle reflections ($hkl = 111, 220$ and 311 for str. II) which are essential for assigning the clathrate structures in mixed-phase systems were not observed. Certainly in light of our data there is no need to propose a structure II clathrate hydrate with an unusual lattice parameter.

Although the XRD powder data have given a good indication of the symmetry and size of the unit cell in the crystal, the detailed structure remains as yet unknown. Some additional information on the methanol monohydrate can be obtained from NMR spectroscopy. The ^2H NMR quadrupole coupling parameters obtained for the water lattice are useful, as these can be used to give information both on the strength of the hydrogen bonds and the dynamics of the water lattice. The ^2H NMR lineshape for a sample of $\text{CH}_3\text{OH} \cdot \text{D}_2\text{O}$ yielded a quadrupole coupling constant χ ($= e^2Qq/h$) of 206.9 kHz and an asymmetry parameter $\eta = 0.09$. These values are very near to those for ice 1h (215 kHz, 0.1¹¹), and are characteristic of a fully hydrogen-bonded network. The χ value is an average for the D_2O and CH_3OD deuterons, as exchange must produce the deuterium-substituted methanol. The small decrease in χ indicates that the O - O distances are, if anything, on average slightly shorter than those in ice 1h. The temperature dependence of the lineshape (fig. 2) gives a rough indication of the rate of the dynamic processes in which water molecules are involved. Above about 140K, the lineshape develops a central component which is a manifestation of slow reorientation of the water molecules within the lattice. A comparison with the lineshapes obtained for pure ice 1h indicates that the water molecules in the methanol hydrate at ~ 150K have the same motional correlation time as those in ice 1h at ~260K. Since the water reorientation in ice is defect-driven, the implied low activation energy for water reorientation in methanol monohydrate must reflect the ease with which defects can be generated. A more detailed analysis of D_2O dynamics is complicated by the fact that besides the water molecules there are two kinds of methanol O-D bonds that must be involved in restricted dynamic processes (see below). Examination of a corresponding $\text{CD}_3\text{OD} \cdot \text{H}_2\text{O}$ (fig. 2, below) sample showed that there are two dynamically inequivalent CD_3 groups, as there are two overlapping powder doublets. Both CD_3 groups show rapid rotation about their 3-fold axes, one of the two shows little or no additional motion, the second shows the presence of another process which formally can be explained by a jump between two positions with ~ 40° between the directions of the CD_3 group symmetry axes. The central line (fig. 2, right) arises from the more mobile OD and HOD deuterons. The NMR measurements show quite clearly that molecular motion is possible at much lower temperatures than in a pure ice lattice.

CONCLUSIONS

On the basis of results reported here it appears unnecessary to propose the existence of a clathrate hydrate of methanol. In vapour-deposited or quenched water - methanol mixtures the crystallization products include mainly methanol monohydrate and ice 1h on the water-rich side of the composition diagram. Methanol seems to act as a catalyst for the direct conversion of glassy ices to ice 1h. On the basis of XRD it is proposed that the methanol monohydrate is tetragonal with unit cell dimensions $a = 4.660$, $c = 13.813$ Å. NMR results indicate that both water and methanol are part of a fully hydrogen-bonded network, but that water reorientation takes place much more easily than in pure ice 1h and in most clathrate hydrates. Finally, one can say that methanol by all accounts remains an inhibitor of hydrate formation.

* Issued as NRCC no:39128

* Permanent adress: Department of Chemistry, Osaka University, Osaka, Japan

[†] Author for correspondence

¹ Sloan, Jr., E. D. "Hydrates of Natural Gas", Marcel Dekker, New York, N. Y. 1991

² Davidson, D. W., Gough, S. R., Ripmeester, J. A., Nakayama, H., Canad. J. Chem. 1981 59, 2587

³ Davidson, D. W., in "Water a Comprehensive Treatise, Franks, F., Ed., Plenum, N. Y., 1973, Vol.2

⁴ Calvert, L. D., Srivastava, P., Acta Crystallogr. Sect. A 1969, 25, S131

⁵ Ripmeester, J. A., Ratcliffe, C. I., J. Phys. Chem. J. Phys. Chem. 1990 94, 8773

⁶ Blake, D., Allamandola, L., Sandford, S., Hudgins, D., Friedemann, F., Science 1991 254, 548

⁷ Davidson, D. W., Handa, Y. P., Ratcliffe, C. I., Ripmeester, J. A., Tse, J. S., Dahn, J. R., Lee, F., Calvert, L. D., Mol. Cryst. Liq. Cryst. 1986, 141, 141

⁸ Wallqvist, A., J. Chem. Phys. 1992 96, 5377

⁹ Vuillard, G., Sanchez, M., Bull. Chem. Soc. Fr. 1961, 1877

¹⁰ Handa, Y. P., Hawkins, R. E., Murray, J. J., J. Chem. Thermodyn. 1984, 16, 623; Y. P. Handa, J. Chem. Thermodyn. 1986, 18, 891

¹¹ Ripmeester, J. A., Ratcliffe, C. I., Klug, D. D., J. Chem. Phys. 1992, 96, 8503

Table 1. Summary of Calorimetric Data ; thermal events are shown in *italics*, phases present in **bold type**

Starting material			
ice (a)	10:1 mixture (a)	1:1 mixture (quenched)	methanol (a)
<hr/>			
ice Ih		liquid mixture	liquid
195K(en)		183K(en; w)	
	179K(en; w)		178K(en)
	Ice Ih + liq 173K(en)	Ice Ih + liq 174K(en)	β phase + liq.
Ice Ic			
	MeOH.H₂O + Ice Ih	MeOH.H₂O + Ice Ih + eutectic mixture	168K(en)
		158K(en,w)	α phase + eutectic mixture 158K(en,w)
	148K(ex, w)		
142K(ex)		MeOH.H₂O + Ice Ih + eutectic mixture (s)	α phase + eutectic mixture (s)
136K(g)	131K(ex)		
		122K(ex)	
Ice (a)	amorphous mixture	112K(g)	
		amorphous mixture	102K(ex) methanol (a)

a = amorphous; ex = exotherm; en = endotherm; w = weak; g = glass transition, s = solid

Figure 1. X-ray powder diffraction patterns for a 1:2 methanol-water mixture obtained at 90K; the sample was annealed for 6 hours at 120K before the other patterns were obtained at the temperatures indicated. The crystalline phases present are: ice Ih (marked on the 180K pattern); methanol monohydrate (marked on the 160K pattern); α and β methanol (marked on the 140K pattern). the amorphous material shows up as broad background scattering especially at low temperatures, liquid as broad background at 180K.

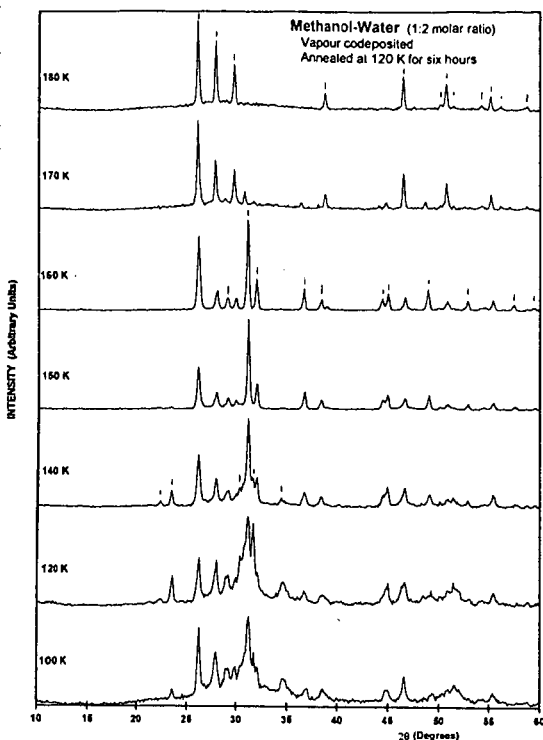


Figure 2. ^2H NMR powder patterns for (right) $\text{CH}_3\text{OH} \cdot \text{D}_2\text{O}$ - temperature dependence; (below) $\text{CD}_3\text{OD} \cdot \text{H}_2\text{O}$ at 140 K experimental and simulated patterns (parameters for outer and inner powder doublets $\chi = 46.83$ kHz, $\eta = 0.04$; $\chi = 37.80$, $\eta = 0.18$)

